

DW DRINKING-WATER WELLS (Data from Kingsbury and Shelton, 2002)

Figure 18. Specific conductance, pH, and dissolved-oxygen concentrations for samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aquifer.

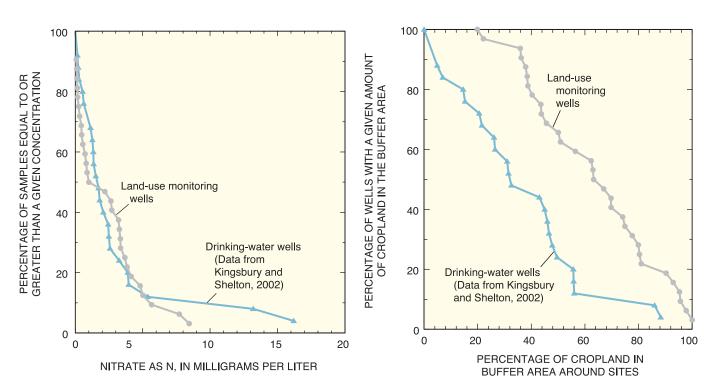


Figure 19. Nitrate concentrations in samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aguifer.

Figure 20. Amount of cropland in buffer areas around agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aguifer.

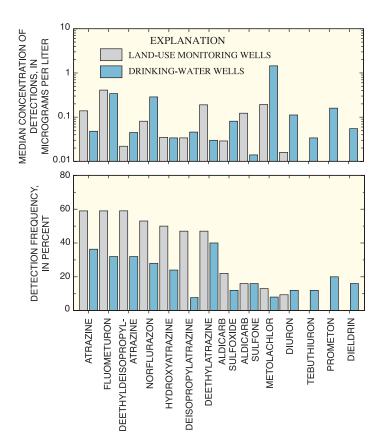


Figure 21. Detection frequency and median concentrations of selected pesticides and degradates detected at concentrations equal to or greater than 0.01 microgram per liter.

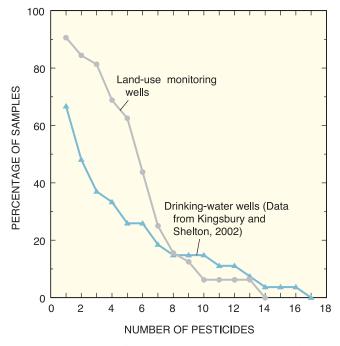


Figure 22. Number of pesticides detected in samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aquifer.

(fig. 20). A number of the samples analyzed for pesticides by HPLC/MS (fluometuron, norflurazon, and aldicarb degradates) from the drinking-water wells exceeded the sample holding time. The concentrations and detection frequencies for these pesticides may be biased low, and the holding time exceedances could contribute to the lower detection frequencies in samples from the drinking-water wells than detection frequencies in samples from the land-use monitoring wells.

Tebuthiuron, prometon, and dieldrin, which have non-agricultural uses, were detected in samples from the drinking-water wells but were not detected above 0.01 µg/L in samples from the land-use monitoring wells. The concentrations of these pesticides were comparable to the concentrations of the pesticides detected that are used on cropland; however, their detection frequency is somewhat lower (fig. 21). Tebuthiuron and prometon are herbicides that are used predominantly for weed control along rights-of-way and roadsides, and they were detected in samples from drinking-water wells having large amounts of urban land use in the buffer areas or that were near railroads and highways (Kingsbury and Shelton, 2002). Although dieldrin had agricultural use until the 1970s, detections only in samples from the drinking-water wells suggest that the principal source of dieldrin to the aquifer is residue remaining from its use for termite control around homes.

No individual pesticide concentrations from either well network exceeded drinking-water standards, but drinking-water standards typically do not exist for degradates, which may have toxicological characteristics similar to the parent pesticide. The potential health effects of mixtures of low-level pesticides and their degradates are not known. A high percentage of samples from both networks contained at least one pesticide. More than 60 percent of samples from the land-use monitoring wells and about 25 percent of samples from the drinking-water wells had five pesticide or pesticide-degradate detections (fig. 22). The high percentage of samples with multiple pesticide detections is a result of the co-occurrence of fluometuron, norflurazon, aldicarb degradates (cotton pesticides), and atrazine and its degradates. Few samples from either network (about 15 percent) had more than eight pesticides in a sample, but the frequency of samples with a large number of detections was greater in the drinking-water wells (fig. 22). The higher percentage of samples with eight or more pesticides and

the greater number of pesticides detected in samples from the drinking-water wells may be a result of the larger contributing areas for these wells than for the land-use monitoring wells. The larger contributing areas for the drinking-water wells likely integrate more land uses and crop types, which increases the maximum number of pesticides detected but generally lowers concentrations (fig. 23).

The total pesticide concentration was more than an order of magnitude higher in the land-use monitoring wells than in the drinking-water wells for 50 percent of samples (fig. 23). The total pesticide concentration was less than 1 μ g/L in 60 percent of the land-use monitoring wells and in about 80 percent of the drinking-water wells (fig. 23). Similar to the number of pesticides detected in a sample, the total pesticide concentration for the two networks converge for about the upper 15 percent of samples. The likelihood of a well having a total pesticide concentration greater than 2 μ g/L (not including the cotton herbicide degradates) was about the same for both networks.

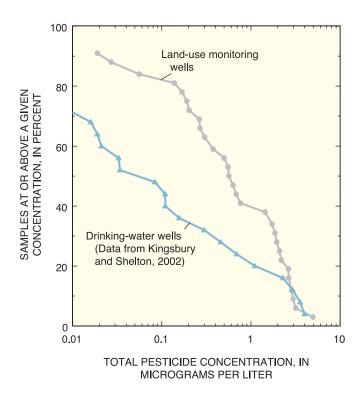


Figure 23. Total pesticide concentration for samples from agricultural land-use monitoring wells and drinking-water wells in the Mississippian carbonate aquifer.

SUMMARY AND CONCLUSIONS

Thirty-two monitoring wells were installed in regolith in the Mississippian carbonate aquifer and sampled for major inorganic constituents, nutrients, and selected pesticides and pesticide degradates to characterize the effect of row-crop agriculture on the quality of recently recharged ground water. Land use and soil characteristics within a 1,640-ft radius buffer area around each well were delineated, and pesticide use was estimated based on crop acreages. A close association among land use, soil characteristics (cropland in areas with well-drained soils), and hydrology in this area limited the analysis of how these factors affect nitrate and pesticide occurrence. The interdependence of these variables in this study suggests that ground-water reconnaissance studies that attempt to relate ground-water quality to factors such as soil properties without considering possible correlation between soil properties and land use may attribute movement of pesticides into ground water to differences in soils, when in fact, differences in land use and pesticide use are related to soil characteristics.

Nitrate concentrations in the land-use monitoring wells generally were low, with a maximum concentration of about 8 mg/L and a median of 1 mg/L. The principal factor affecting nitrate concentrations was dissolved-oxygen concentrations. Low dissolvedoxygen concentrations in wells likely indicate longer average ground-water residence times, slow rates of recharge, or some degree of confinement in the regolith. Ratios of chloride (which is conserved in ground water) to nitrate suggest that nitrate concentrations in at least a third of the samples were affected by denitrification. Although nitrate concentrations were not correlated to the amount of cropland in the buffer areas, a correlation between nitrate and total pesticide concentrations suggests that cropland is the probable source of nitrate to the these wells. Nitrate concentrations in this study generally were lower than concentrations measured in similar agricultural land-use well networks sampled for the National Water-Quality Assessment Program throughout the Nation.

Agricultural land in the Eastern Highland Rim typically occurs in areas with well-drained soils and low organic matter content, which likely contributes to the frequent detection of the most heavily used pesticides in the land-use monitoring wells. With the exception of glyphosate, which sorbs tightly to soil, pesticides with the highest use, such as fluometuron, atrazine, and their degradates, were detected most fre-

quently and at the highest concentrations. Fluometuron and atrazine were detected in 83 and 70 percent, respectively, of the samples from wells that had applications of these pesticides in the surrounding buffer areas. Those samples without atrazine and fluometuron detections, but with estimated use in buffer areas, were from wells with dissolved-oxygen concentrations less than 1.5 mg/L. Generally, pesticide concentrations were less than 1 µg/L, and the maximum concentration measured was 3.21 µg/L of demethylnorflurazon, a degradate of the cotton herbicide norflurazon. The highest concentrations of pesticides generally were associated with short average ground-water residence time as indicated by high dissolved-oxygen concentrations and low calcite saturation indices. Pesticide degradates usually were detected in association with the parent pesticide, and concentrations generally were comparable to or greater than the parent pesticide concentrations.

Nitrate concentrations in samples in this study generally were lower than in samples from similar well networks in agricultural areas across the country; however, pesticides were detected more frequently in samples in this study. For example, atrazine and its degradate, deethylatrazine, were detected in 62 and 47 percent, respectively, of samples in this study and were detected in about 25 percent of the 851 wells sampled for agricultural land-use studies conducted by the National Water-Quality Assessment Program. In those study areas with atrazine use greater than in the lower Tennessee River Basin, atrazine was detected in about 30 percent of the samples. Cotton pesticides were detected much more frequently in this study, but many of the study areas nationwide had small amounts of cotton acreage.

Similar nitrate and pesticide concentrations in samples from these shallow monitoring wells and samples collected in an earlier study from deeper drinking-water wells completed in bedrock indicate that the Mississippian carbonate aquifer is susceptible to nonpoint-source contamination associated with cropland. Nitrate concentrations generally were low in both well networks, and concentrations greater than 5 milligrams per liter were infrequent. The finegrained texture of the regolith likely slows the rate of nitrate transport throughout much of the area and allows for some denitrification to occur, keeping concentrations low. Pesticide detection frequencies and maximum concentrations were higher in the land-use monitoring wells than in the drinking-water wells; however, the median concentrations of pesticides

detected in both networks were similar. The lower frequency of detection in the drinking-water wells may result from a smaller percentage of cropland in the contributing areas of these wells. Pesticides with noncropland uses were detected in the drinking-water wells at lower frequencies than pesticides used on cropland, but at similar concentrations. Similarities in water quality of ground water collected from the landuse monitoring wells and the drinking-water wells probably reflect the karst hydrology of the aquifer, which allows for substantial movement of nonpointsource contaminants away from agricultural areas once water has moved through the regolith to conduits in bedrock. Rapid movement of nonpoint-source contaminants also can occur when recharge enters the conduit flow system through sinkholes or macropores where the regolith is thin.

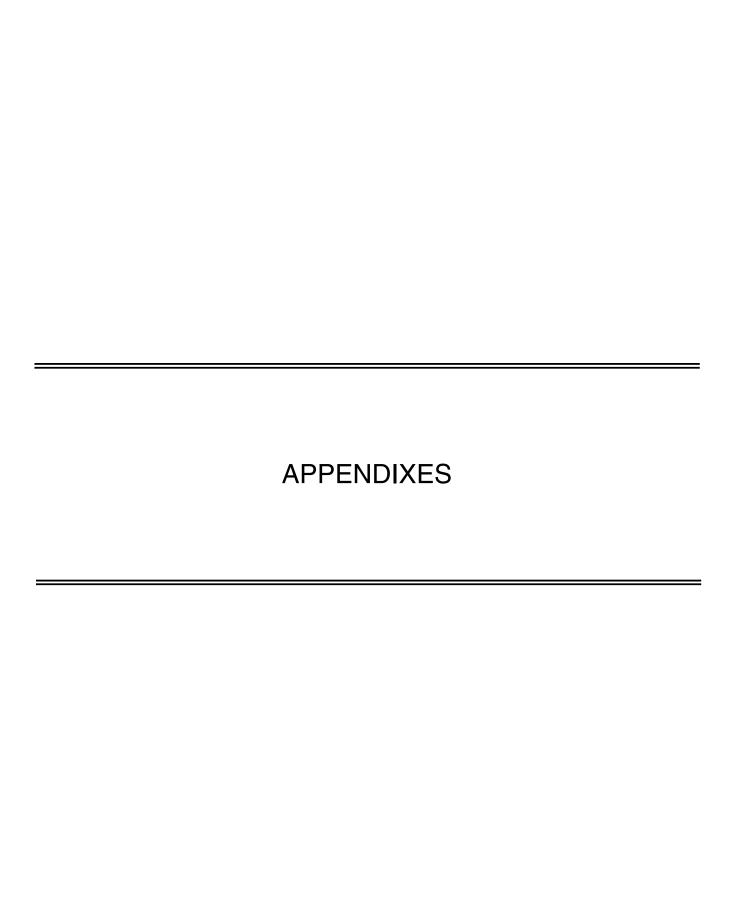
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Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use

[MRL, minimum reporting level; µg/L, micrograms per liter; CAS, chemical abstracts reference number; H, herbicide; I, insecticide; F, fungicide; Degr., pesticide degradate; N/A, not applicable; --, no CAS number; pesticides in italics were analyzed before analytical method approval, and data in this report are provisional; *, pesticides denoted with an asterisk have had low or inconsistent recoveries throughout method development, and concentrations always are reported as estimated; pesticides denoted with a "+" were analyzed at the U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kansas]

Compound	Common name	MRL, in μg/L	CAS number	Use
-	Pesticides detected			
2,4-D methyl ester	N/A	0.086	1928-38-7	Н
3(4-chlorophenyl) methyl urea	N/A	0.092	1897-46-6	H-Degr.
Acetochlor	Acenit, Guardian, Harness	0.002	34256-82-1	Н
Aldicarb*	Temik	0.082	116-06-3	I
Aldicarb sulfone*	Standak, aldoxycarb	0.16	1646-88-4	I-Degr.
Aldicarb sulfoxide*	Temik sulfoxide	0.027	1646-87-3	I-Degr.
Atrazine	Aatrex	0.001	1912-24-9	Н
Deethylatrazine*	N/A	0.002	6190-65-4	H-Degr.
De is opropy latrazine *	N/A	0.074	1007-28-9	H-Degr.
Deethyl de is opropylatrazine *	N/A	0.06	3397-62-4	H-Degr.
Hydroxyatrazine	N/A	0.193	2163-68-0	H-Degr.
Bentazon*	Basagran, Adagio, Galaxy, Storm	0.019	25057-89-0	Н
Carbaryl*	Sevin	0.003	63-25-2	I
Carbofuran*	Furadan	0.003	1563-66-2	I
Diphenamid	Dymid, Enide, Rideon, Dyfen	0.058	957-51-7	Н
Diuron	DCMU, Diurex, Aguron, Karmex	0.079	330-54-1	Н
Fluometuron	Cortoran, Lanex, Cottonex, Flo-met	0.062	2164-17-2	Н
Demethylfluometuron+	N/A	0.05		H-Degr.
3-(trifluromethyl) aniline (TFMA)+	N/A	0.05		H-Degr.
Imazethapyr*	Pursuit, Pursuit DG	0.088	81335-77-5	Н
Metalaxyl	Apron, Subdue, Ridomil	0.057	94-81-5	F
Methiocarb*	Draza, Mesurol, Slug-geta	0.08	57837-19-1	I
Metolachlor	Dual, Pennant	0.002	51218-45-2	Н
Methomyl*	Nudrin, Lannate, Lanox	0.077	2032-65-7	I
Metribuzin	Sencor, Lexone	0.004	21087-64-9	Н
p,p'-DDE	N/A	0.006	72-55-9	I-Degr.
Norflurazon	Solicam, Telok, Evital, Zorial	0.077	27314-13-2	Н
Demethylnorflurazon+	N/A	0.05		H-Degr.
Pendimethalin	Prowl, Stomp	0.004	40487-42-1	Н
Prometon	Pramitol, Princep	0.018	1610-18-0	Н
Trifluralin	Treflan, Gowan	0.002	1582-09-8	Н
Siduron	Tupersan, Trey	0.093	1982-49-6	Н
Simazine	Princep	0.005	122-34-9	Н
Sulfometuron-methyl	Oust, DPX-T5648	0.039	74222-97-2	Н

Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use—Continued

Compound	Common name	MRL, in μg/L	CAS number	Use
	Pesticides not detected			
2,4-D	Aqua Kleen, Weedone-2,4-DP	0.077	94-75-7	Н
2,6-Diethylaniline	N/A	0.003	579-66-8	H-Degr.
3-Hydroxycarbofuran	N/A	0.062	16655-82-6	I-Degr.
3-Ketocarbofuran*	N/A	0.072	16709-30-1	I-Degr.
3-(trifluromethyl)phenylurea (TFMPU)+	N/A	0.05		H-Degr.
2,4-DB	Butyrac, Butoxone, Legumex D	0.054	94-82-6	Н
Acifluorfen, sodium salt	Tackle, Blazer	0.062	62476-59-9	Н
Alachlor	Lasso, Bronco	0.002	15972-60-8	H
alpha-BHC	HCH-alpha	0.002	319-84-6	I
Bendiocarb	Ficam, Tattoo	0.061	22781-23-3	I
Benfluralin	Balan, Benefin	0.002	1861-40-1	Н
Benomyl	Benlate	0.022	17804-35-2	F
Bensulfuron-methyl	Londax	0.048	83055-99-6	Н
Bromacil*	Bromax, Hyvar, Uragon	0.081	314-40-9	Н
Bromoxynil*	Bromanil, Buctril, Torch	0.057	1689-84-5	Н
Butylate	Sutan +	0.002	2008-41-5	Н
Chloramben methyl ester*	Amiben, methyl ester	0.114	7286-84-2	Н
Chlorimuron-ethyl	Classic	0.037	90982-32-4	Н
Chlorothalonil*	Bravo, Forturf	0.048	1897-45-6	Н
Chlorpyrifos	Lorsban, Dursban	0.004	2921-88-2	I
Clopyralid	Stinger, Lontrel	0.041	1702-17-6	Н
Cyanazine	Bladex	0.004	21725-46-2	Н
Cyanazineamide+	N/A	0.05		H-Degr.
Cycloate*	Ro-Neet, Marathon	0.054	1134-23-2	Н
Dacthalmonoacid	DCPA Monoacid	0.072	887-54-7	H-Degr.
DCPA	Dacthal	0.002	19719-28-9	Н
Diazinon	Spectracide	0.002	333-41-5	I
Dicamba	Banvel, Marksman, Clarity	0.096	1918-00-9	Н
Dichlorprop	Seritox 50, Weedone	0.05	120-36-5	Н
Dieldrin	Dieldrin, Panoram D-31	0.001	60-57-1	I
Dimethenamid	Frontier	0.05	87674-68-8	Н
Dinoseb	DNPB, Caldon, Dynamite	0.043	88-85-7	Н
Disulfoton	Di-Syston	0.017	298-04-4	I
EPTC	Eradicane, Eptam	0.002	759-94-4	Н
Ethalfluralin	Sonalan	0.004	55283-68-6	Н
Ethoprop	Mocap	0.003	13194-48-4	I
Fenuron	Beet-Klean, Fenidim	0.074	101-42-8	Н

Appendix 1. Pesticides and pesticide degradates analyzed, common name, and use—Continued

Compound	Common name	MRL, in μg/L	CAS number	Use
-	Pesticides not detected—Continued			
Flumetsulam*	DE 498, XRD 498	0.087	98967-40-9	Н
Fonofos	Dyfonate	0.003	944-22-9	I
Glyphosate+	Round-up	0.1	1071-83-6	Н
Imazaquin*	Image 1.5LC; Scepter 1.5L	0.103	81335-37-7	Н
Imidacloprid	Admire, Gaucho, Merit	0.106	105827-78-9	I
Lindane	Isotox	0.004	58-89-9	I
Linuron	Lorox	0.002	330-55-2	Н
Malathion	Cythion	0.005	121-75-5	I
MCPA	Bordermaster, Metaxon, Rhomene	0.058	86-50-0	Н
MCPB*	Tropotox, Can-Trol, PDQ	0.062	94-74-6	Н
Methomyl oxime*	N/A	0.01	16752-77-5	I-Degr.
Azinphos-methyl*	Guthion	0.001	13749-94-5	I
Methyl parathion	Penncap-M	0.006	298-00-0	I
Metsulfuron-methyl *	Escort, Gropper, Ally	0.114	74223-64-6	Н
Molinate	Ordram	0.004	2212-67-1	Н
Napropamide	Devrinol	0.003	15299-99-7	Н
Neburon	Granurex, Herbalt, Kloben	0.075	555-37-3	Н
Nicosulfuron	Accent, Accent DF	0.065	111991-09-4	Н
Oryzalin	Ryzelan, Surflan, Dirimal		19044-88-3	Н
Oxamyl	Vydate L, Thioxamyl	0.016	23135-22-0	I
Oxamyl oxime*	N/A	0.064	30558-43-1	I-Degr.
Parathion	Phoskil	0.004	56-38-2	I
Pebulate	Tillam	0.004	1114-71-2	Н
cis-Permethrin	Pounce, Ambush	0.005	54774-45-7	I
Phorate	Thimet	0.002	298-02-2	I
Picloram	Tordon, Amdon, Grazon	0.071	191802-1	Н
Prometryn+	Caparol	0.05	7287-19-6	Н
Pronamide	Kerb	0.003	23950-58-5	Н
Propachlor	Ramrod	0.007	1918-16-7	Н
Propanil	Stam, Stampede	0.004	709-98-8	Н
Propargite	Comite	0.013	2312-35-8	I
Propiconazole	Tilt, Orbit, Banner, Proconazole, Wocosin	0.064	60207-90-1	F
Propoxur	Baygon, PHC, Suncide, Unden	0.059	114-26-1	I
Tebuthiuron	Graslan, Spike, Perflan	0.01	34014-18-1	Н
Terbacil*	Sinbar, DPX-D732, Geonter	0.007	5902-51-2	Н
Terbufos	Counter	0.013	13071-79-9	I
Thiobencarb	Bolero	0.002	28249-77-6	Н
Triallate	Far-Go	0.001	2303-17-5	Н
Tribenuron-methyl*	Express, tribenuron methyl ester, DPX-L5300	0.068	101200-48-0	Н
Triclopyr	Garlon, Curtail, Redeem, Remedy	0.101	55335-06-3	Н

Appendix 2. Chlorofluorocarbon concentrations, calculated atmospheric partial pressures, and model recharge dates for sampled wells

[temp., temperature; °C, degrees Celsius; pg/kg, picograms per kilogram; pptv, parts per trillion by volume; CFC, chlorofluorocarbon; Contam., CFC concentrations in samples were greater than air-water atmospheric equilibrium concentrations; Modern, CFC concentrations indicative of 2000 atmospheric concentrations]

-				Elev.		Concentration in solution,		Calculated Atmospheric			Model CFC recharge dates,		
			Recharge	e (feet	in pg/kg			partial pressure, in pptv			in years		
Well	Sampling		temp.	above									
number		Time					CFC-113			CFC-113	CFC-11		CFC-113
35	05/25/00	1450	16.2	640	546.5	261.5	64.9	270.2	546.8	78.6	1990.5/ 1998.0	1997.0	1990.5
35	05/25/00	1515	16.2	640	542.3	245.2	67.2	268.2	512.7	81.5	1990.0/ 1998.5	1992.5	1991.0
35	05/25/00	1525	16.2	640	539.3	251.8	66.9	266.6	526.5	81.1	1989.5	1994.0	1991.0
14	05/31/00	1555	13.8	822	525.3	261.0	62.4	231.6	493.0	66.7	1986.5	1990.5	1988.5
14	05/31/00	1615	13.8	822	527.1	267.8	64.5	232.4	505.8	68.9	1986.5	1991.5	1988.5
14	05/31/00	1620	13.8	822	518.9	241.9	62.5	228.8	456.8	66.7	1986.0	1988.0	1988.5
11	06/06/00	1635	14.8	860	976.5	320.0	74.5	453.8	633.6	84.3	Contam.	Contam.	1992.0/ 1997.0
11	06/06/00	1640	14.8	860	544.2	269.4	66.8	252.9	533.4	75.6	1988.0	1994.5	1989.5
11	06/06/00	1700	14.8	860	547.9	271.3	66.2	254.6	537.2	74.9	1988.0	1995.5	1989.5
7	06/05/00	1450	13.7	950	655.1	301.2	95.3	288.7	569.0	101.7	Modern	Modern	Contam.
7	06/05/00	1510	13.7	950	649.3	289.8	94.7	286.2	547.5	101.0	Modern		Contam.
7	06/05/00	1520	13.7	950	639.4	266.4	88.8	281.8	503.2	94.7	Modern		Modern
25	05/24/00	1100	17.5	550	24.2	56.4	0.0	12.7	124.5	0.0	1961.0	1969.5	<1955
25	05/24/00		17.5	550	23.3	50.3	0.0	12.2	111.0	0.0	1960.5	1968.5	<1955
25	05/24/00		17.5	550	23.5	52.1	0.0	12.4	115.0	0.0	1960.5	1969.0	<1955
23	03/24/00	1120									1700.5	1707.0	<1 <i>733</i>
20	05/25/00	1015	14.7	580	520.4	295.4	71.1	238.1	576.2	79.2	1987.0	Modern	1990.5
20	05/25/00	1030	14.7	580	4,010.7	279.4	67.7	1,835.3	544.9	75.3	Contam.	1997.0	1989.5
20	05/25/00	1050	14.7	580	1,384.0	306.6	73.3	633.3	598.1	81.6	Contam.	Contam.	1991.0
12	06/07/00	1220	15.1	765	750.1	285.6	63.3	352.7	571.2	72.6	Contam.	Modern	1989.0
12	06/07/00	1250	15.1	765	849.6	348.1	79.0	399.5	696.2	90.6	Contam.	Contam.	Modern
12	06/07/00	1300	15.1	765	909.2	301.6	74.9	427.5	603.2	85.9	Contam.	Contam.	1994.0
13	06/01/00	1445	15.0	705	560.0	260.2	69.8	261.4	516.9	79.3	1989.0	1992.5	1990.5
13	06/01/00		15.0	705	562.2	266.2	71.8	262.4	528.8	81.7	1989.0	1994.0	1991.0
13	06/01/00		15.0	705	567.3	262.7	70.2	264.8	521.8	79.8	1989.0	1994.0	1991.0
10	50,01,00	12.00									1,0,0	1,,,,,,	1,,0.5
33	05/22/00	1530	13.4	540	215.0	155.3	25.4	91.9	284.9	26.3	1973.0	1978.0	1981.0
33	05/22/00	1550	13.4	540	219.8	129.5	23.7	93.9	237.6	24.4	1973.0	1975.5	1980.0
33	05/22/00	1600	13.4	540	229.3	133.4	26.2	98.0	244.7	27.0	1973.5	1976.0	1981.0